Dithienylcyclopentene optical switches

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Chapter 5

Dithienylethenes for Non-Destructive Readout, Towards Single Molecule Switching

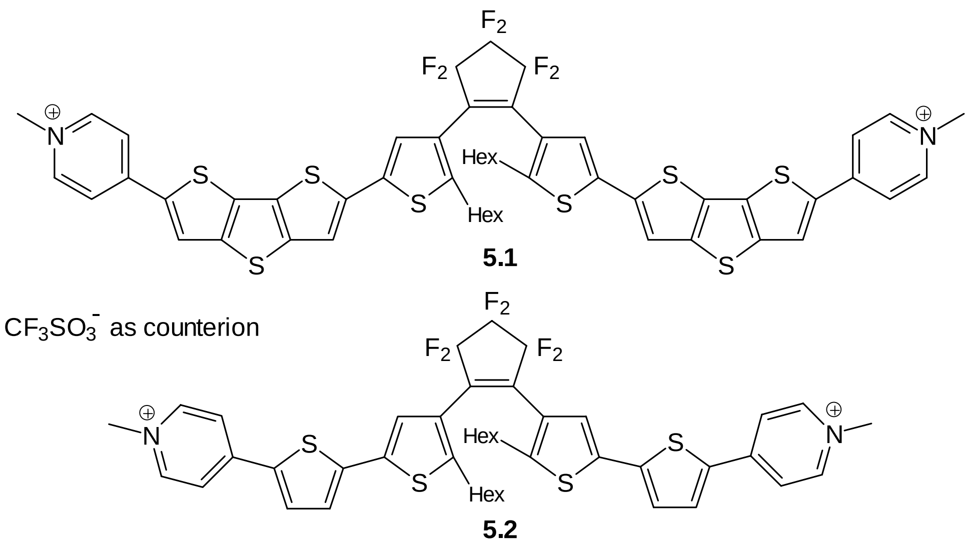
5.1 Single molecule switching

Single molecule spectroscopy[1] allows the observation of optical spectra of individual complexes without the ensemble averaging over static intercomplex disorder, thus directly revealing the properties of the electronic structure of the excited states. Up to now, processes in which the behavior of single molecules can be controlled are very rare. Basché *et al*. reported single molecule optical switching of terrylene embedded in a *p*-terphenyl host crystal.[2] They were able to induce controlled frequency jumps of single terrylene molecules by light. The controlled manipulation and switching of single atoms and molecules evokes the prospect of ultra high-density data storage. However, photochemical switching between two states of a single molecule has not yet been demonstrated. To accomplish single molecule switching first the molecule must be addressed selectively within an array of molecules. This can be achieved by embedding the molecules in polymers, crystals, or by dispersion as isolated molecules on surfaces. Single molecule switching also requires: (a) photochemical switching between two states; (b) a non-destructive readout procedure. For a practical optical memory the wavelength required for read-out should not interfere with the switching process, because otherwise the stored information would be erased. In other words a nondestructive read-out is required. One possible way to accomplish this is by gated reactivity. This has already been discussed in Chapter 2.4.3. Another way is to use fluorescence as non-destructive read-out method. Fluorescence is highly sensitive. For this end single molecule fluorescence spectroscopy is a method that has been successfully applied in recent years for the detection of single guest molecules in crystalline and amorphous matrices.[1] Single molecules are usually detected by this straightforward technique, introduced by Orrit *et al.*,[3] which has become a standard method in the field of high-resolution optical spectroscopy. It is possible to use our dithienylethenes for single molecule switching, if (a) there is a difference in fluorescence emission between the open and closed form of the diarylethene, and (b) the fluorescence excitation wavelength does not interfere with the switching process of the diarylethene.

In this chapter the photochromic properties and the synthesis of dithienylethenes functionalized with oligothiophenes combined with pyridines will be discussed. These were initially developed for single molecule spectroscopy in collaboration with physicists from the University of Leiden.

5.2 Synthesis

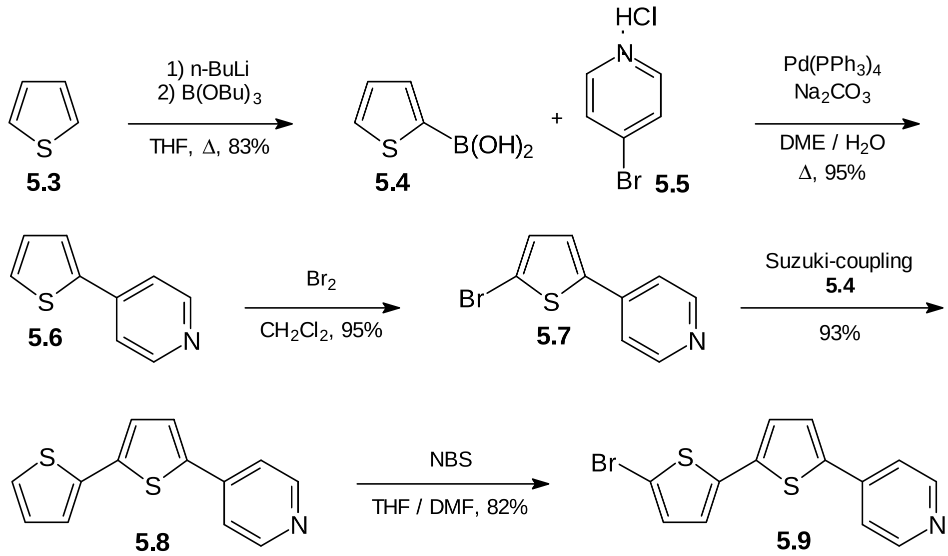
Lehn and coworkers synthesized two potential switches functionalized with oligothiophenes with pyridinium ion tails (**5.1** and **5.2**, Scheme 5.1) that were strongly fluorescent in their open form.[4] The closed form of these compounds, however, emitted only weakly. The absorption bands used for the fluorescence excitation are inactive with respect to the opening-closing photoreactions. This behavior was not observed for the non-methylated derivatives of **5.1** and **5.2**.



Scheme 5.1 *Fluorescent dithienylethenes with pyridinium ion tails.*

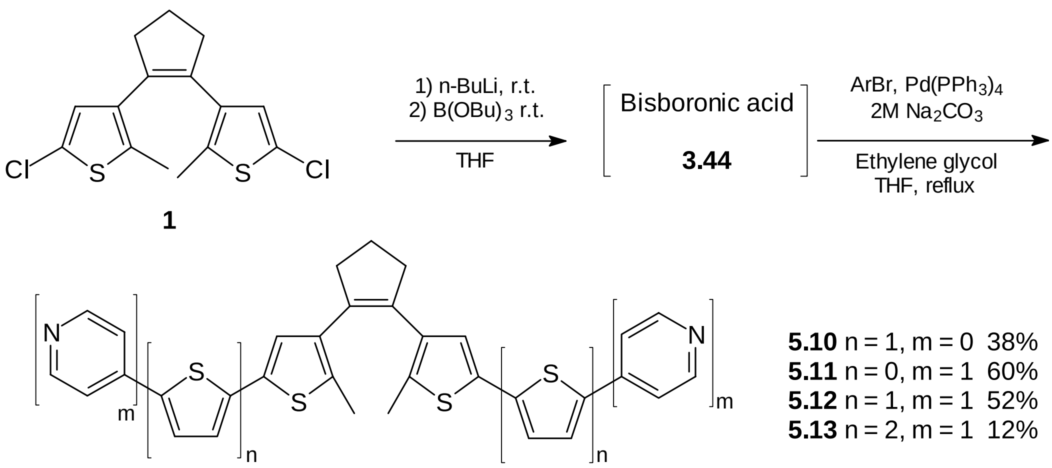
This looked promising for non-destructive read-out for single molecule switching. In order to achieve some fast results we decided to synthesize a series of dithienylcyclopentenes in which the conjugated system has been extended by use of an oligothiophene and pyridine combination (Scheme 5.3). These compounds were all prepared via the Suzuki reaction, as described in chapter 3, starting from **1** and the corresponding aryl bromides (Scheme 5.2). The analytical data for these compounds are in accord with those described in literature.[5,6]

The aryl bromides were obtained via a straightforward synthesis. First thiophene **5.3** was lithiated by n-butyllithium at room temperature and quenched with tributylborate in THF at ambient temperature to provide 2-thienylboronic acid **5.4** after acidic work-up.[5] The 4-bromopyridine HCl-salt **5.5** and compound **5.4** were coupled via a Suzuki coupling with $Pd(PPh_3)_4$ as palladium source and sodium carbonate as base in a mixture of H_2O and DME to provide **5.6** in 95% yield.[5] Bromination of this compound afforded **5.7** in 93% yield. This bromide derivative was used in order to synthesize **5.8**. Another Suzuki reaction under the same conditions (*vide supra*) with **5.4** and **5.7** resulted in 2,2'-bisthiophene-5-(pyridin-4'-yl) **5.8** in 93% yield. After bromination[6] of the latter compound, **5.9** was obtained in 57% overall yield starting from **5.3**.

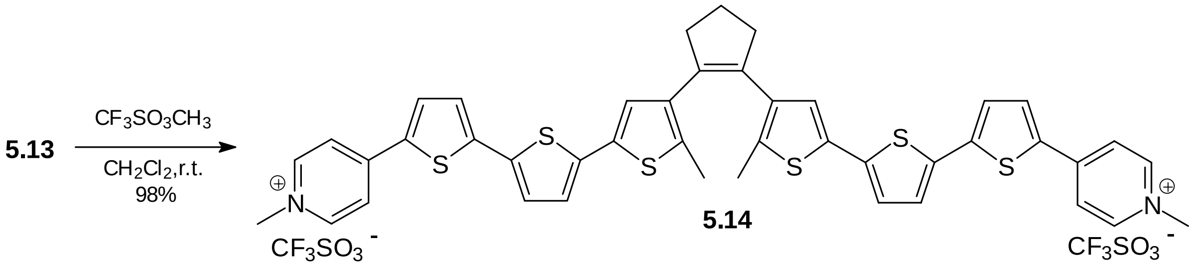


Scheme 5.2 *Synthesis of the aryl bromides.*

The desired diarylethenes were synthesized via the Suzuki-reaction (Scheme 5.3). First, **1** was lithiated with BuLi in THF at room temperature, and then allowed to react with $B(OBu)_3$ to provide a bis-boronic ester **3.44**. This compound was used directly in the Suzuki reaction without any work-up because it was found that these boronic acids easily hydrolyse during isolation. For this Suzuki cross coupling reaction $Pd(PPh_3)_4$ was added as a palladium source, Na_2CO_3 as base, THF as solvent and several drops of ethylene glycol were added as cosolvent. Afterwards the compounds were purified by column chromatography and obtained in a yield ranging from 12 to 60 %. The low yields were due to the difficulties in purification. Especially **5.13** was very hard to purify, because the Suzuki reaction did not proceed completely. Therefore the aryl bromide **5.9** and **5.13** had to be separated, which turned out to be very difficult. In the Suzuki reaction the amount of mono-substituted compounds was less than 5%.



Scheme 5.3 *Synthesized series of dithienyl oligothiophene derivatives.*



Scheme 5.4 *N-methylation of* ***5.13****.*

The pyridine moieties of compound **5.13** were methylated with methyl trifluoromethanesulfonate at ambient temperature to provide **5.14** in almost quantitative yield (Scheme 5.4). This compound was synthesized to determine the influence of N-methylation on the photochemical behavior. The diarylethene derivatives were characterized by ^{1}H, ^{13}C NMR and mass (EI).

5.3 Photochromic properties

The synthesized compounds (Scheme 5.3) were examined with UV-Vis spectroscopy before and after irradiation in order to elucidate their photochromic behavior. Therefore solutions (~10^{-5}M) of all the compounds (Scheme 5.3) were prepared in various solvents. The absorption spectrum of a solution of **5.13** in benzene (2.15 x 10^{-5}M) is shown in Figure 5.1. The molecule has a very strong absorption band at 399 nm. The absorption band with a maximum at 402 nm arises chiefly from the 2,2'-bisthiophene-5-(pyridin-4'-yl) group attached to the diarylethene unit in **5.13**. The chromophore alone, as in compound **5.8** in benzene (1.32 x 10^{-4}M) showed the same broad absorption band with λ_{max} = 351 nm as a result of a π-π^{*}-transition.[7] Compound **5.13** has an extra thiophene compared to **5.8**, resulting in an extended π-conjugated system. As a consequence λ_{max} of the absorption band showed a red shift compared to **5.8**.

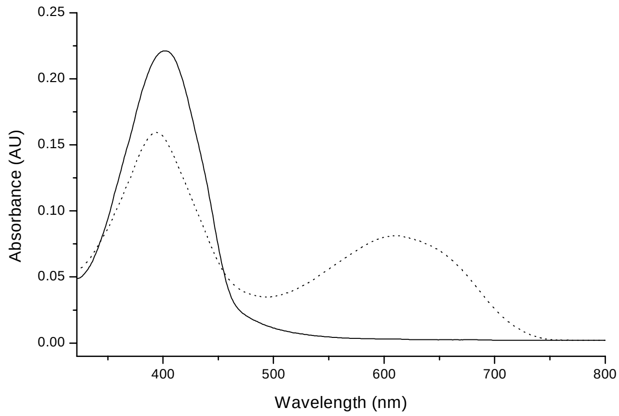
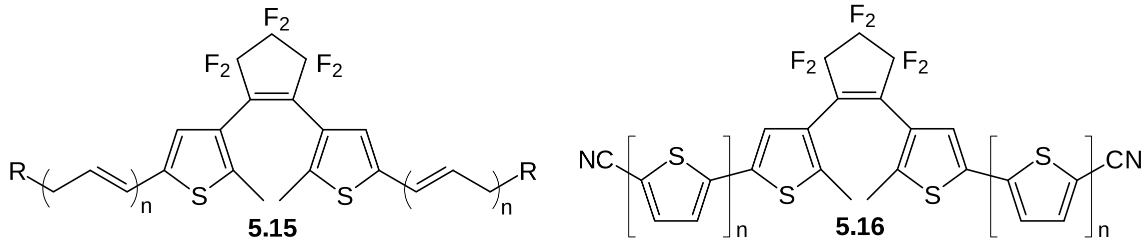


Figure 5.1 *UV-Vis spectra of* ***5.13*** *in benzene before* (—) *and after irradiation* (---) *(photo stationary state, PSS) at λ > 380 nm.*

Irradiation of a benzene solution of **5.13** at λ = 313 nm with a high pressure mercury lamp (200W) did not result in any change in the absorption spectrum, nor did irradiation at λ = 405 nm, λ = 365 nm or λ = 340 nm lead to any change in our experimental setup. Only when λ > 380 nm is used as exciting wavelength did an absorption in the visible region appear (λ_{max} = 609 nm). Compared to other ring-closing reactions of dithienylcyclopentenes, the quantum yield for ring closure was low. Attempts to accomplish ring-opening of **5.13** failed, as prolonged irradiation at λ > 520 nm did not result in any change of the UV-Vis spectra. Apparently the switch stayed in the ring-closed from. This was also confirmed by ^{1}H NMR studies of **5.13** in benzene-d_6. After irradiation with λ > 380 nm a second singlet for the methyl groups appeared at 2.35 ppm, which was assigned to the closed form. After irradiation with various filters in the visible region, also no change could be observed in the ^{1}H NMR spectrum. This phenomenon has been observed before by Martin *et al*. (**5.15**)[8] and Irie *et al.*[9] (**5.16**), who showed that the quantum yield for ring-opening dramatically decreased with increasing π-conjugation length (Scheme 5.5).



Scheme 5.5 *Diarylethene derivatives, which showed a dramatically decrease in the quantum yield of the ring opening reaction*.

In case of the diarylethenes described by Martin (**5.15)** there is no ring-opening reaction observed when n ≥ 4. These observations were explained as follows: (a) The excited-state lifetime of the closed form decreases with increasing conjugation length or (b) the excitation density at the central switch scaffold is reduced, which should lead to a decrease in the reaction rate.

Compound **5.12** with one thiophene less than **5.13** was examined next. A degassed solution in benzene (1.21 x 10^{-5}M) showed absorptions at 303 nm and 367 nm (Figure 5.2, left). After irradiation at λ = 313 nm a new absorption band with λ_{max} at 589 nm appeared (Figure 5.2, left). The ring-opening reaction proceeded smoothly on irradiation with λ > 540 nm. This process is fully reversible and can be repeated several times without observable degradation. Compound **5.11** showed similar behavior. The absorption spectrum of **5.11** in degassed benzene (8.2 x 10^{-5}M) showed a maximum at 285 nm and a shoulder at 320 nm (Figure 5.2, right). After irradiation at λ = 313 nm an absorption with λ_{max} at 546 nm appeared in the visible region due to the closed form. Upon irradiation with λ > 540 nm this 546 nm band completely disappeared, indicating that the ring opening of the closed form is quantitative. Apparently, the switching cycle of **5.11** is also fully reversible because it could be repeated several times without noticeable degradation of the closed or open form.

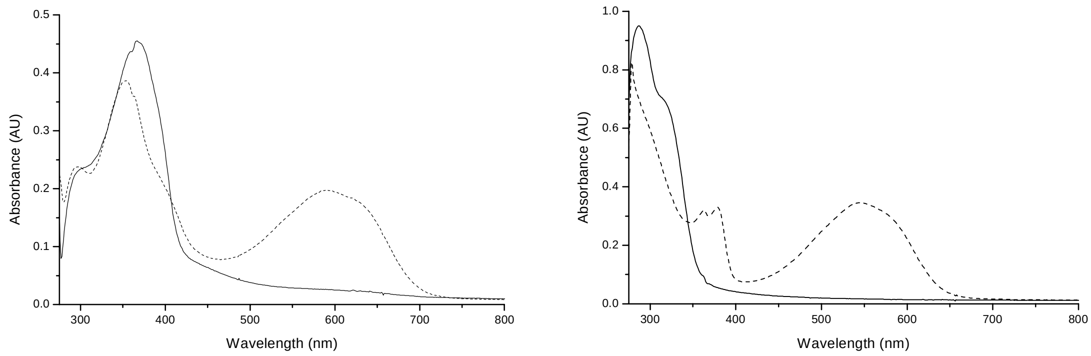


Figure 5.2 *(left) Absorption spectra of* ***5.12*** *in benzene before* (—) *and after irradiation* (---) *at λ = 313 nm for 10 min. (right) UV-Vis spectra of* ***5.11*** *in benzene before* (—) *and after irradiation* (---) *at λ = 313 nm for 5 min.*

Finally bisthiophene switch **5.10** in cyclohexane (1.86 x 10^{-4}M) was subjected to the same irradiation measurements. The UV-VIS spectra of the open and closed from of **5.10** are depicted in Figure 5.3. The absorption maxima of the open form are 290 nm and 322 nm, whereas after irradiation at λ = 313 nm the closed form has an absorption maximum of 543 nm. Ring opening with λ > 520 nm proceeded also in this case without any problems.

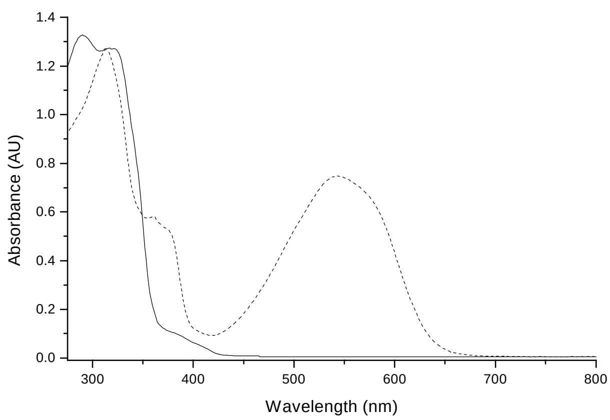


Figure 5.3 *UV-Vis spectra of* ***5.10*** *in cyclohexane before* (—) *and after irradiation* (---) *at λ = 313 nm for 8 min.*

From these experiments it appears that in case of extended π-conjugation length, as in compound **5.13**, both the ring closure reaction and the ring opening reaction proceed sluggishly if at all. In the case of **5.13** the ring closure reaction takes place, though under more strenuous irradiation conditions than usually applied. The ring closure reaction does not proceed anymore, an observation which is in agreement with earlier findings (*vide supra*). Only one thiophene less in the side chain provides the right conditions for smooth ring opening and ring closing reactions, as in the case of compounds **5.12**, **5.11** and **5.10**. The influence of the π-conjugation length is also evident when the absorption maxima of the open and closed forms are considered. A longer π-conjugated system results in an increased red shift of the absorption maximum.

5.4 Fluorescence behavior

The highly fluorescent solution of **5.13** and earlier findings by Lehn *et al*.[4] (*vide supra*) prompted us to investigate the fluorescence properties of this compound. The measurements were performed with a degassed benzene solution (2.2 x 10^{-6}M). Fluorescence measurements showed that the open form has a strong emission at 464 and 495 nm when excited at λ = 399 nm, *i.e*. at its absorption maximum. However, the closed form of **5.13** (λ > 380 nm, pss) showed hardly any fluorescence irrespective of the excitation wavelength (Figure 5.4). The fluorescence of **5.13** can thus photochemically be changed from a pronounced to almost zero emission. This is similar to the observations that were made by Lehn.[4] It is not clear at the moment which structural or conjugation effects are responsible for this dramatic change in fluorescence. This change in fluorescence could be used in order to achieve nondestructive read-out when the excitation does not induce a ring opening- or ring closure reaction.

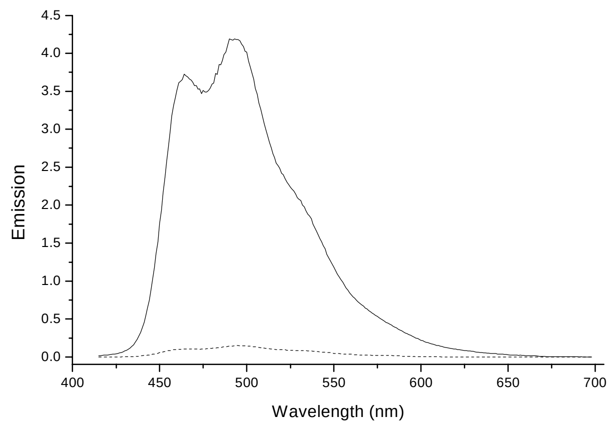


Figure 5.4 *Emission spectra of **5.13** in benzene before* (—) *and after irradiation* (---) (pss) *at λ > 380 nm (λ_{exc} = 402 nm).*

The fluorescence spectrum of a degassed benzene solution of compound **5.12** (1.21 x 10^{-6}M) is depicted in Figure 5.5. The open form of compound **5.12** showed very weak fluorescence (λ_{exc} = 367 nm) compared to compound **5.13** (Figure 5.4) and, moreover, the closed form showed almost the same fluorescence emission. The ring-closure reaction, however, competes with the fluorescence emission, because after excitation the solution of the sample was slightly blue colored, indicative of the closed form. This was indeed confirmed by UV-Vis spectroscopy.

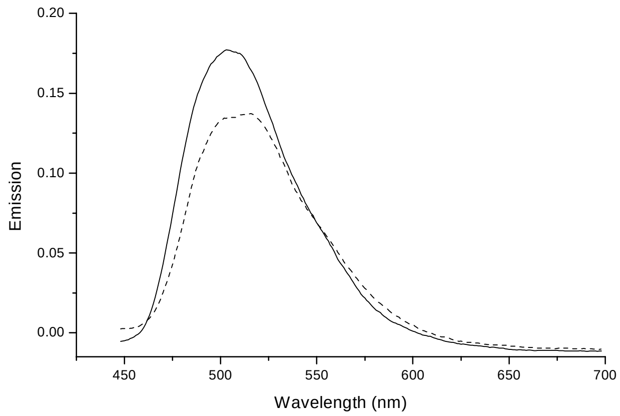


Figure 5.5 *Emission spectra of **5.12** in benzene before* (—) *and after irradiation* (---) (pss) *at λ = 313 nm (λ_{exc} = 367 nm).*

Excitation of compound **5.11** (8.2 x 10^{-6}M) did not give emission at all, and apparently compound **5.11** only undergoes a ring closure reaction after excitation at λ = 285 nm or 320 nm. Also the ring-closed form was non-fluorescent. The same was found in case of compound **5.10**. After excitation the compound gave ring closure and did not show any emission. A solution of 5-methyl-2,2'-bisthiophene (2.0 x 10^{-5}M) in benzene showed an absorption maximum at 312 nm. In contrast to compound **5.10**, after excitation at λ = 312 nm fluorescence was observed with an emission maximum at λ_{max} = 372 nm (Figure 5.6).

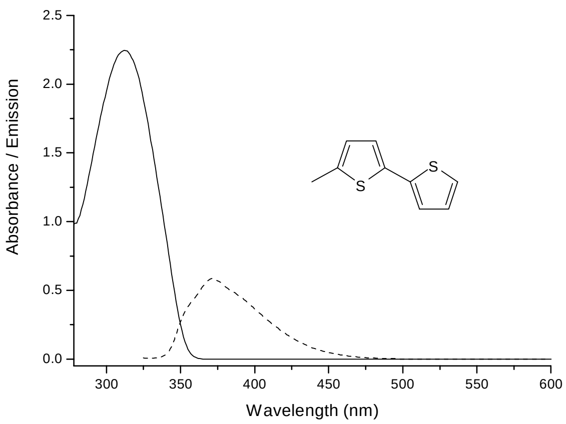


Figure 5.6 *Absorption (2.0 x 10^{-4}M)* (—) *and emission spectrum (2.0 x 10^{-5}M)* (---) *of 5-methyl-2,2'-bisthiophene in benzene (λ_{exc} = 312 nm).*

In conclusion, photocyclization is favored for diarylethenes with shorter chains of aryl groups. This means a less extended π-conjugated system and therefore the absorption maximum of the open form shifts to the blue. Fluorescence is favored for more highly substituted analogues with a more extended π-conjugated systems and a red-shifted excitation wavelength.

5.5 Photochromic and fluorescence behavior of N-methylated and N-protonated pyridine substituted-diarylethene molecular switches

For pyridine-containing dithienylcyclopentenes it has been shown that there are large differences in the electronic and fluorescence spectra.[4,7] Compared to compound **5.13**, the absorption maximums of the methylated derivative **5.14** in MeOH (2.6 x 10^{-5}M) is shifted by 68 nm to λ = 467 nm for the open form of **5.14** (Figure 5.7).

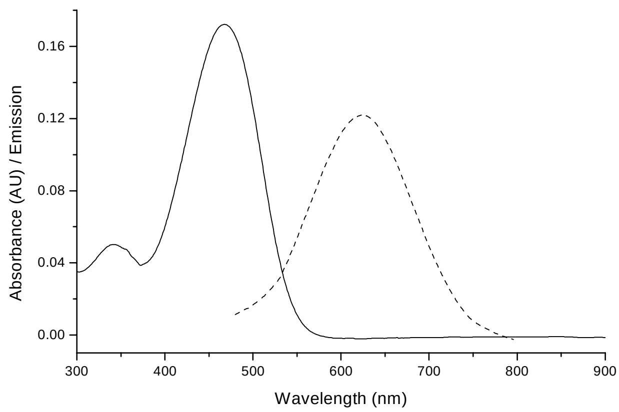


Figure 5.7 *Absorption spectrum* (—) *and emission spectrum* (---) *of* ***5.14*** *in methanol* (λ_{exc} *= 467 nm).*

Irradiation of this solution did not result in a ring-closure reaction, irrespective of the wavelength used. The reason for the fact that **5.14** does not show any switching behavior is probably due to the lower excitation density at the central ring scaffold further enhanced by the N-methylated pyridine, making fluorescence more favored. Excitation of this compound at λ = 467 nm resulted in a very weak emission, compared to **5.13** at λ = 620 nm at the same concentration (Figure 5.7). For compounds **5.10 – 5.13** a decrease in photocyclization was observed in favor of the fluorescence in that order, in other words with increasing π-conjugation. For compound **5.14** a decrease in photocyclization does not give a big increase in fluorescence emission.

In order to get a quick insight into the photochromic and fluorescence behavior of compounds **5.12** and **5.11** when they are positively charged, the compounds were protonated in situ with excess trifluoroacetic acid (TFA). A drop of TFA was therefore added to the solution of **5.12** in benzene (1.21 x 10^{-6}M) in a quartz cuvet. The absorption maximum of the open form shifted from 367 nm to 433 nm (Figure 5.8, left). When the solution was subsequently irradiated at λ > 460 nm, the ring-closed form appeared with λ_{max} = 661 nm. Apparently, although protonation of **5.12** with TFA caused a pronounced red shift of the absorption maxima of the open and the closed form, it does not inhibit the photochemical ring-closing reaction as has been observed for the N-alkylated derivative of **5.13**. Protonation of **5.12** has also a pronounced effect on the fluorescent properties. A proton is now directly bound to the nitrogen atom through the lone pair and this results in further increase of the intensity of the emission, but without a clear shift in wavelength.[7] Emission from the open form of **5.12** is enhanced by protonation, but after conversion to the closed form by irradiation at λ = 313 nm, the emission intensity was reduced by a factor of 2 compared to that of the open form, but was still more pronounced than the non-protonated closed form. The presence of the closed form probably reduced the emission intensity.

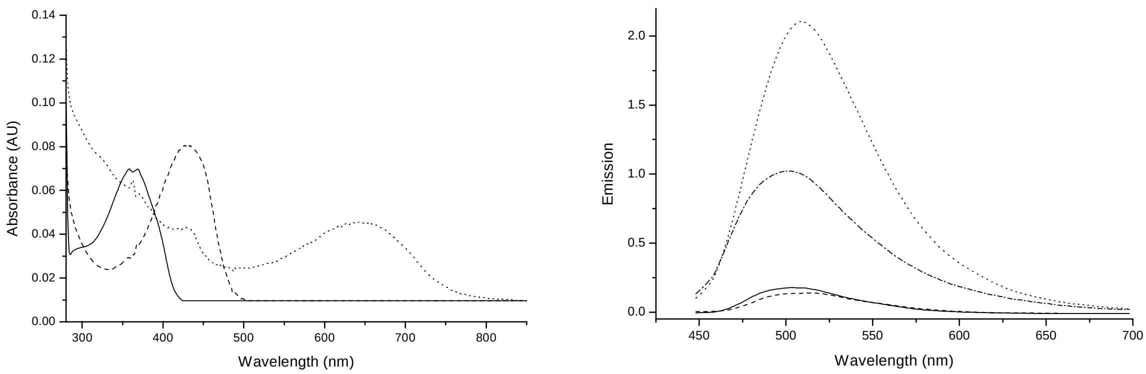


Figure 5.8 (left) *Absorption spectra of **5.12** in benzene before* (—) *and after addition of TFA* (---), *and of a protonated **5.12** after irradiation at λ = 365 nm for 2 min.* (···) *(right). Emission spectra of **5.12** at λ_{exc} = 367 nm before* (—) *and after irradiation* (---) *at λ = 313 nm for 10 min., and protonated **5.12** (TFA) at λ_{exc} =433 nm before* (···) *and after irradiation* (·–·–) *at λ = 365 nm for 2 min.*

Protonation of **5.11** with TFA also resulted in a red shift of the absorption maxima of the open form to 323 nm and 367 nm (Figure 5.9). After irradiation of **5.11** at λ = 365 nm the protonated closed form was obtained with λ_{max} = 643 nm. The absorption maximum of the closed form is shifted almost 100 nm on protonation. In contrast to **5.12** for which protonation gave a significant increase in emission intensities, both the open and closed form of **5.11** remain essentially non-fluorescent after protonation. The open form mainly underwent ring closure after excitation, this was confirmed by UV-Vis.

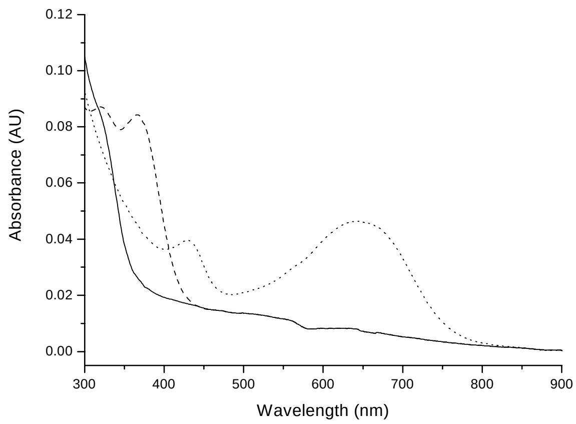


Figure 5.9 *Absorption spectra of **5.11** in benzene before* (—) *and after addition of TFA* (---), *and protonated solution irradiated at λ = 365 nm for 4 min.* (···).

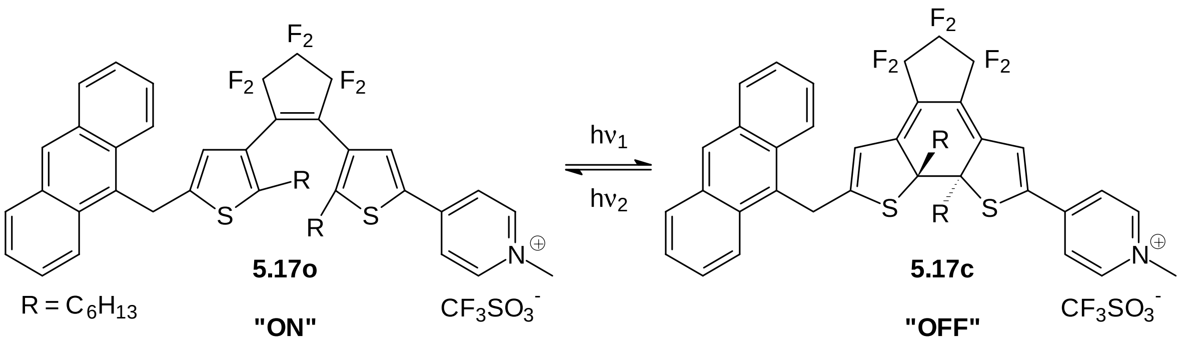
Rather than using protonated pyridines for which the degree of protonation cannot be determined with certainty, it is recommended to synthesize the N-methylated versions of **5.11** and **5.12**. This would make it possible to perform some coloring-bleaching cycles, which is not possible for the protonated compound because of the excess of TFA. The protonation of the pyridines is also an equilibrium, thus it can also be that non-protonated species are switching back to the open form.

The N-methylated form of **5.13** and **5.14**, showed no ring closure whatsoever, but showed also hardly any fluorescence emission. The protonated forms of **5.12** and **5.11** do undergo ring closure after irradiation, but at the moment no clear conclusions can be drawn about the ring opening reaction, because the presence of an excess of TFA caused degradation of the compounds during prolonged irradiation and therefore the ring opening reaction did not proceed completely. Compound **5.12**, showed more pronounced fluorescence emission compared to its non-protonated form. Compound **5.11**, however, did not show any fluorescence emission upon excitation but only ring closure was found. The same trend is observed for the protonated species as with the non-protonated species. An extended π-conjugated system leads to preferentially fluorescence emission or solely fluorescence emission as in case of compound **5.14**.

5.6 Effective single molecule switching

Fluorescence can be used as a nondestructive readout for single molecule switching if (a) there is a difference in fluorescence emission between the open and closed form of the diarylethene, and (b) the fluorescence excitation wavelength does not interfere with the switching process of the diarylethene. Compound **5.13** showed a pronounced difference in fluorescence emission in the open and closed form. The question remained if the compound also met the second requirement e.g. separate absorption bands for excitation and ring closure. Therefore the wavelength dependence for fluorescence and ring closure upon excitation of the main absorption band in the visible region has been investigated in Leiden. The following things were observed. Irradiation in the range λ = 300-380 nm only resulted in fluorescence emission and did not result in the ring closure of **5.13**. Ring closing is most effective when irradiation occurs in the range λ = 420-470 nm. Furthermore it was established that the molecules underwent degradation, on average after 7 switching cycles. This means that on an average only 7 fluorescence events can take place. For single molecule switching at least 1000 fluorescence events have to be collected in order to achieve a reasonable signal to noise ratio, before switching or degradation might occur. It can thus be concluded that **5.13** is not suitable for single molecule switching.

Another approach to switches that can be independently be addressed for switching or fluorescence was reported by Effenberger.[10] A novel dithienylethene-bridged donor-acceptor system (**5.17o**) was developed which is capable of reversibly ON/OFF photoswitchable (photo-induced) charge separation (Scheme 5.6). The methylene spacer effectively decoupled both the donor and the acceptor. This allows one to address individually either of these chromophores.

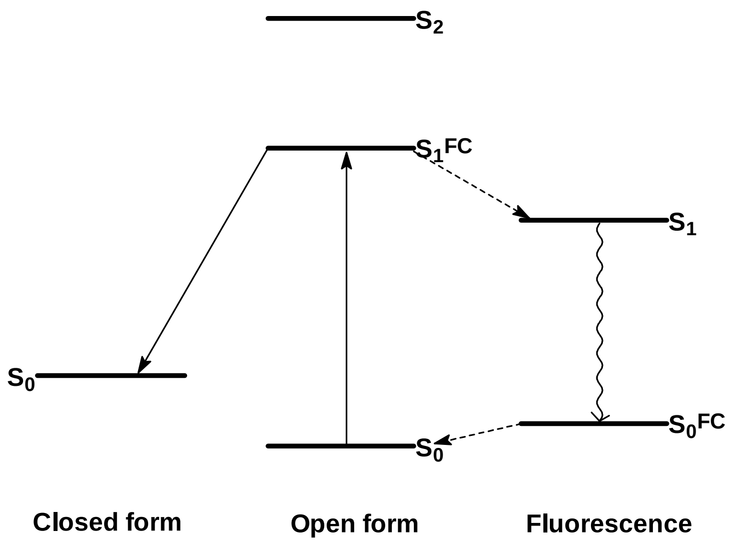


Scheme 5.6 *Photoswitchable (photo-induced) charge separation*.

In the open form (**5.17o**) photoexcitation of the anthracene resulted in a complete intramolecular electron transfer from the donor (anthracene) to the acceptor (pyridinium unit). However, after photoexcitation of the donor in the closed form (**5.17c**) no charge separation was observed. This transformation is reversible. The fact that no charge separation was observed in the closed form demonstrated that improved conjugation due to the closed form was not decisive for an intramolecular photo-induced electron transfer. The model of a "conjugation switch" can therefore not be used for this system. Compound **5.17o** showed fluorescence behavior, whereas **5.17c** displayed no fluorescence, indicating complete quenching of the anthracene fluorescence. This system would be more effective in single molecule switching.

5.7 Conclusions

In symmetrically-substituted dithienylcyclopentenes described in this chapter photocyclization or fluorescence takes place upon excitation to the lowest excited state S_1. The processes that can occur, are depicted in Scheme 5.7. This is a simplified scheme in order to visualize the processes. After excitation of the compound it can either undergo ring closure to the closed form or go back to the ground state of the open form after fluorescence emission. The process depends on the nature of the aryl groups attached to the dithienylcyclopentene scaffold. Photocyclization is favored for dithienylcyclopentene derivatives possessing fewer aryl groups thus a system with a less extended π-conjugated system, blue-shifting the wavelength needed for cyclization. Fluorescence is favored for more highly substituted analogues with a more π-conjugated system and a red-shifted excitation wavelength. TFA-protonated analogues with a more π-conjugated system show more pronounced fluorescence emission than their non-protonated analogues. Also the absorption maximum after photocyclization of these TFA-protonated analogues showed a tremendous redshift. Compound **5.13** cannot be used for single molecule switching due to too fast degradation of the system.



Scheme 5.7 *Simplified Jablonski diagram for excitation behavior of the synthesized switches*.

5.8 Acknowledgements

I am grateful to dr. Adriaan J. Minnaard for synthesizing the aryl bromides described in this chapter. Furthermore I would like to thank dr. E. Groenen, dr. A.M. van Oijen and drs. R. Verberk from the Physics Department at the University of Leiden for making the effort of testing the possibilities for single molecule switching of compound **5.13**.

5.9 Experimental section

All measurements have been carried out at room temperature. The samples were irradiated in a 1cm quartz cuvet for UV-Vis measurements and in 5 mm pyrex tubes for NMR experiments, using a 200W mercury lamp (Oriel) with the appropriate band-pass or high-pass filters (Andover corporation). The fluorescence measurements were performed on a SPF-500C spectrofluorometer manufactured by SLM Aminco. The determination of an exact mass of **5.12** and **5.13** appeared impossible due to the problems with the ionization of the compounds. For more general remarks see Chapter 3.6.

2-Thienylboronic acid (5.4): Thiophene (17 g, 0.2 mol) and anhydrous THF (150 ml) were placed in a 1l three-neck flask. After cooling to –6°C n-BuLi (100 ml, 0.16 mol, 1.6M) was added very carefully via a syringe. The mixture was allowed to stir at r.t. for 45 min. Then the mixture was cooled to –65°C and $B(OnBu)_3$ (54 ml, 0.2 mol) was added at once via a syringe. The temperature rose to –30°C. The mixture was warmed to r.t. and H_2O was added. The organic layer was separated from the aqueous layer and washed with saturated NH_4Cl (2 x 25 ml). A significant fraction of product could be recovered form the aqueous layer by extraction with diethyl ether (3 x 50 ml). These organic layers were combined and washed with saturated NH_4Cl (2 x 25 ml). The product was then extracted form the organic layer by cold 2M aqueous NaOH (3 x 70 ml), and the combined aqueous layers were acidified at 0°C to pH = 1 by slow addition of conc. HCl. The product precipitated as a white powder, which was collected on a glass filter and dried under vacuum at r.t. A white solid was finally obtained (17 g, 83%). m.p. 115°C (lit 123°C sol. Pet ether);[11] ^{1}H NMR (300MHz, CD_3OD) δ_H 7.04 (s, 1H), 7.51 (s (br), 2H); ^{13}C NMR (75.4 MHz, CD_3OD) δ_C 128.79 (d), 132.15 (d), 136.52 (d); MS (EI): 128 [M^+].

4-Thiophen-2-yl-pyridine (5.6): Na_2CO_3 (8.5 g, 80 mmol) was dissolved in H_2O (20 ml) and DME (30 ml) and 4-bromopyridine-HCl-salt (7.76g, 40 mmol) were successively added, upon which a white precipitate was formed. This suspension was heated to reflux while 2-thienylboronic acid **5.4** (7.04 g, 55 mmol) was added. Immediately the suspension turned brown where upon $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol) was added. This mixture was refluxed for 3 h. After cooling to r.t. the DME was removed in vacuo. The aqueous layer was extracted with diethyl ether (4x). The organic layers were combined and the product was extracted from these layers with 1M aqueous HCl (150 ml). The acidic aqueous layer was then adjusted to pH ~ 10 by addition of aqueous NaOH (33%) solution while cooling in an ice-bath. The product was recovered from the basic water layer by extraction with diethyl ether (4 x 50 ml). The combined organic layers were dried (Na_2SO_4) and after evaporation of the solvent a white solid (6.13g, 95%) was obtained. m.p. 88°C (lit 87-88°C);[6] ^{1}H NMR (300MHz, $CDCl_3$) δ_H 7.10 (dd, J = 4.2 Hz, 1H), 7.38 (dd, J = 0.9 Hz, 1H), 7.43-7.48 (c, 3H), 8.56 (d, J = 5.1 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 119.79 (d), 125.26 (d), 127.13 (d), 128.36 (d), 141.06 (s), 141.27 (s), 150.27 (d); MS (EI): 161 [M^+].

2-Bromothiophene-5-(pyridin-4'-yl) (5.7): **5.6** (4.0 g, 24.8 mmol) was dissolved in DMF (40 ml) and NBS (4.4 g, 34.7 mmol) in DMF (15 ml) was added dropwise at 0°C together with a few drops of Br_2. After 8h aqueous HCl (1M) was added and the mixture was extracted with EtOAc. After an acid-base extraction the organic layers were dried (Na_2SO_4). After evaporation of the solvent a light-brown solid (4.43g, 95%) was obtained. m.p. 148°C (lit 152-154, sol. EtOH);[12] ^{1}H NMR (300MHz, $CDCl_3$) δ_H 7.03 (d, J = 3.9 Hz, 1H), 7.19 (d, J = 4.2 Hz, 1H), 7.31 (d, J = 6.3 Hz, 2H), 8.54 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 114.29 (s), 119.26 (d), 125.46 (d), 131.19 (d), 140.32 (s), 142.36 (s), 150.37 (d); HRMS calcd. for $C_9H_6NS^{81}Br$ 240.938, found 240.939.

4-[2,2'-Bisthiophene-5-(pyridin-4'-yl)] (5.8): This reaction was carried out as described for **5.6**, starting with **5.7** (0.5g, 2.08 mmol), 2-thienylboronic acid (5.4) (0.43 g, 3.33 mmol), $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol), Na_2CO_3 (0.32g, 3 mmol), DME (4 ml) and H_2O (2 ml). The product was obtained as a yellow solid (0.47 g, 93%). ^{1}H NMR (300MHz, $CDCl_3$) δ_H 7.03 (dd, J = 3.6 Hz, 1H), 7.16 (d, J = 4.2 Hz, 1H), 7.23 (dd, J = 1.2 Hz, 1H), 7.26 (dd, J = 1.2 Hz, 1H), 7.39 (d, J = 3.6 Hz, 1H), 7.42 (d, J = 6.0 Hz, 2H), 8.56 (d, J = 6.3 Hz, 2H); MS (EI): 243 [M^+].

5'-Bromo-[2,2'-bisthiophene-5-(pyridin-4'-yl)] (5.9): This reaction was carried out as described for **5.7**, starting with a solution of **5.18** (3.0 g, 12.3 mmol) in DMF (20 ml), and NBS (2.85 g, 17.6 mmol) in THF (20 ml). An orange-brown solid was obtained (3.25 g, 82%). m.p. 150°C (lit 153°C, sol EtOH)[6] ^{1}H NMR (300MHz, $CDCl_3$) δ_H 6.97 (d, J = 3.9 Hz, 1H), 7.00 (d, J = 3.6 Hz, 1H), 7.11 (d, J = 3.9 Hz, 1H), 7.26 (dd, J = 1.2 Hz, 1H), 7.39 (d, J = 3.6 Hz, 1H), 7.42 (d, J = 6.0 Hz, 2H), 8.56 (d, J = 6.3 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 111.96 (s), 119.43 (d), 124.42 (d), 124.94 (d), 126.12 (d), 130.80 (d), 138.08 (s), 139.86 (s), 140.80 (s), 150.35 (d); HRMS calcd. for $C_{18}H_8NS_2Br$ 320.928, found 320.927.

General procedure for the Suzuki-reactions:

1,2-Bis(5'-boronyl-2'-methylthien-3'-yl)cyclopentene (3.44): Compound **1** (70 mg, 0.2 mmol) was dissolved in anhydrous THF (8 ml) under a nitrogen atmosphere, and n-BuLi (0.31 ml of 1.6M solution in hexane, 0.5 mmol) was added at once using a syringe. This solution was stirred for 30 min at r.t., and B(n-OBu)$_3$ (0.18 ml, 0.6 mmol) was added at once. The resulting solution was stirred for 1 h at r.t. and was used directly in the Suzuki cross coupling-reactions without any workup because boronic acid **3.44** is hydrolysed during isolation.

1,2-Bis(5'-(thiophen-2-yl)-2'-methylthien-3'-yl)cyclopentene (5.10): 2-Bromothiophene (0.04 ml, 0.4 mmol) was dissolved in THF (5 ml) and after addition of $Pd(PPh_3)_4$ (15 mg, 0.012 mmol), the solution was stirred for 15 min at r.t.. Then aqueous Na_2CO_3 (1 ml, 2M) and 6 drops of ethylene glycol were added, and the resulting two-phase system was heated in an oil bath till reflux (60°C). The solution of **3.34** was added dropwise by a syringe in a few min. After addition was complete, the reaction mixture was refluxed for 2 h, and then allowed to cool to r.t.. Diethyl ether (50 ml) and H_2O (50 ml) were added, and the organic layer was collected and dried (Na_2SO_4). After evaporation of the solvent the product was purified by column chromatography (SiO_2, hexane) to gave a purple solid (32 mg, 38%). ^{1}H NMR (300MHz, $CDCl_3$) δ_H 1.95 (s, 6H), 2.01-2.11 (m, 2H), 2.80 (t, *J* = 7.5 Hz, 4H), 6.88 (s, 2H), 6.96 (dd, *J* = 3.9 Hz, *J* = 3.3 Hz, 2H), 7.04 (dd, *J* = 0.6 Hz, 2H), 7.14 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 14.30 (q), 22.93 (t), 38.47 (t), 122.90 (d), 123.66 (d), 124.48 (d), 127.64 (d), 133.00 (s), 133.98 (s), 134.50 (s), 136.25 (s), 137.74 (s); HRMS calcd for $C_{23}H_{20}S_4$ 424.045, found 424.042.

1,2-Bis(5'-(pyridin-4''-yl)-2'-methylthien-3'-yl)cyclopentene (5.11) The same procedure was used as described for **5.10**, starting from **1** (1.97g, 5.97 mmol), and n-BuLi (9.3 ml of 1.6M solution in hexane, 0.15 mol), B(*n*-OBu)$_3$ (4.83 ml, 1.8 mmol), 4-bromopyridine.HCl (2.32 g, 0.12 mol), $Pd(PPh_3)_4$ (0.41 g, 0.35 mmol), aqueous Na_2CO_3 (15 ml, 2M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO_2, methanol/ CH_2Cl_2 = 1/20) gave a green solid (1.48 g, 60%). ^{1}H NMR ($CDCl_3$, 300MHz) δ_H 2.04 (s, 6H), 2.06-2.16 (m, 2H), 2.87 (t, *J* = 7.2 Hz, *J* = 7.8 Hz, 4H), 7.36 (d, *J* = 5.7 Hz, 4H), 8.53 (d, *J* = 5.1 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 14.45 (q), 22.77 (t), 38.24 (t), 119.08 (d), 126.20 (d), 134.60 (s), 136.35 (s), 136.91 (s), 137.20 (s), 141.22 (s), 149.81 (d); HRMS calcd for $C_{25}H_{22}N_2S_2$ 414.122, found 414.121.

1,2-Bis(5'-[2-thienyl-5-(pyridin-4'-yl)]-2'-methylthien-3'-yl)cyclopentene (5.12): The same procedure was used as described for **5.10**, starting from **1** (70 mg, 0.2 mmol), and n-BuLi (0.31 ml of 1.6M solution in hexane, 0.5 mmol), B(*n*-OBu)$_3$ (0.18 ml, 0.6 mmol), **5.7** (0.064 g, 0.4 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.12 mmol), aqueous Na_2CO_3 (1 ml, 2M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO_2, hexane/ ethyl acetate = 1/2) gave a green solid (60 mg, 52 %). ^{1}H NMR (300MHz, $CDCl_3$) δ_H 2.01 (s, 3H), 2.03-2.13(m, 2H), 2.83 (t, *J* = 7.2 Hz, *J* = 7.8 Hz, 4H), 6.98 (s, 2H), 7.09 (d, *J* = 3.9 Hz, 2H), 7.46 (d, *J* = 3.6 Hz, 2H), 7.52 (d, *J* = 6.0 Hz, 4H), 8.55 (d, *J* = 5.4 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 14.40 (q), 33.53 (t), 38.39 (t), 119.32 (d), 123.93 (d), 125.21 (d), 126.10 (d), 132.40 (s), 134.66 (s), 135.13 (s), 136.52 (s), 138.68 (s), 139.60 (s), 141.10 (s), 150.22 (d); MS (DEI): 578 [M^+].

1,2-Bis(5'-[2,2'-bisthiophene-5-(pyridin-4'-yl)]-2'-methylthien-3'-yl)cyclopentene (5.13): The same procedure was used as described for **5.10**, starting from **1** (107 mg, 0.33 mmol), n-BuLi (0.52 ml of 1.6M solution in hexane, 0.83 mmol), B(*n*-OBu)$_3$ (0.27 ml, 1 mmol), **5.9** (0.21g, 0.66 mmol), $Pd(PPh_3)_4$ (0.023 g, 0.20 mmol), aqueous Na_2CO_3 (1 ml, 2M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO_2, methanol/ CH_2Cl_2/Et_3N = 1/20/1%) and subsequent trituration in CH_2Cl_2/ hexane gave a yellow solid (30 mg, 12 %). m.p. decomp. > 210°C, ^{1}H NMR (300MHz, $CDCl_3$) δ_H 2.00 (s, 6H), 2.02-2.12 (m, 2H), 2.83 (t, *J* = 7.2 Hz, *J* = 7.8 Hz, 4H), 6.92 (s, 2H), 7.00 (d, *J* = 3.6 Hz, 2H), 7.16 (d, *J* = 3.6 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 2H), 7.50 (d, *J* = 4.2 Hz, 2H), 7.57 (d, *J* = 5.4 Hz, 4H), 8.58 (d, *J* = 6.6 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 14.35 (q), 22.91 (t), 38.34 (t), 105.32 (d), 119.31 (d), 123.56 (d), 124.41 (s), 124.77 (d), 124.92 (d), 126.22 (d), 132.40 (s), 134.53 (s), 134.59 (s), 134.66 (s), 136.39 (s), 137.51 (s), 139.10 (s), 141.03 (s), 150.10 (d); MS (DEI): 742 [M^+].

1,2-Bis(5'-[2,2'-bisthiophene-5-(pyridin-4'-yl)]-2'-methylthien-3'-yl)cyclopentene (5.14): Compound **5.13** (5.4 mg, 7.3 μmol) was dissolved in CH_2Cl_2 (3 ml) and methyl trifluoromethane sulfonate (2.1 μl, 19μmol) was added. The solution immediately turned red and a solid precipitated. After stirring for 1 h at room temperature the suspension was filtered over a glass filter and the solid material rinsed with CH_2Cl_2 and dried in vacuo to gave a red solid (7.7 mg, 98%). ^{1}H NMR (300MHz, $CDCl_3$) δ_H 1.91 (s, 6H), 2.01-2.11 (m, 2H), 2.79 (t, *J* = 6.9 Hz, *J* = 7.5 Hz, 4H), 4.21 (s, 6H), 7.02 (s, 2H), 7.07 (d, *J* = 4.2 Hz, 2H), 7.33 (d, *J* = 4.2 Hz, 2H), 7.37 (d, *J* = 4.5 Hz, 2H), 7.98 (d, *J* = 3.9 Hz, 2H), 8.10 (d, *J* = 6.9 Hz, 4H), 8.60 (d, *J* = 6.9 Hz, 4H).

5.10 References and notes

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